Thermochemical Heat Storage for Baseload Concentrated Solar Power Generation

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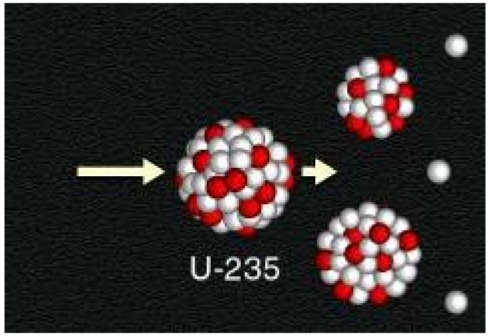
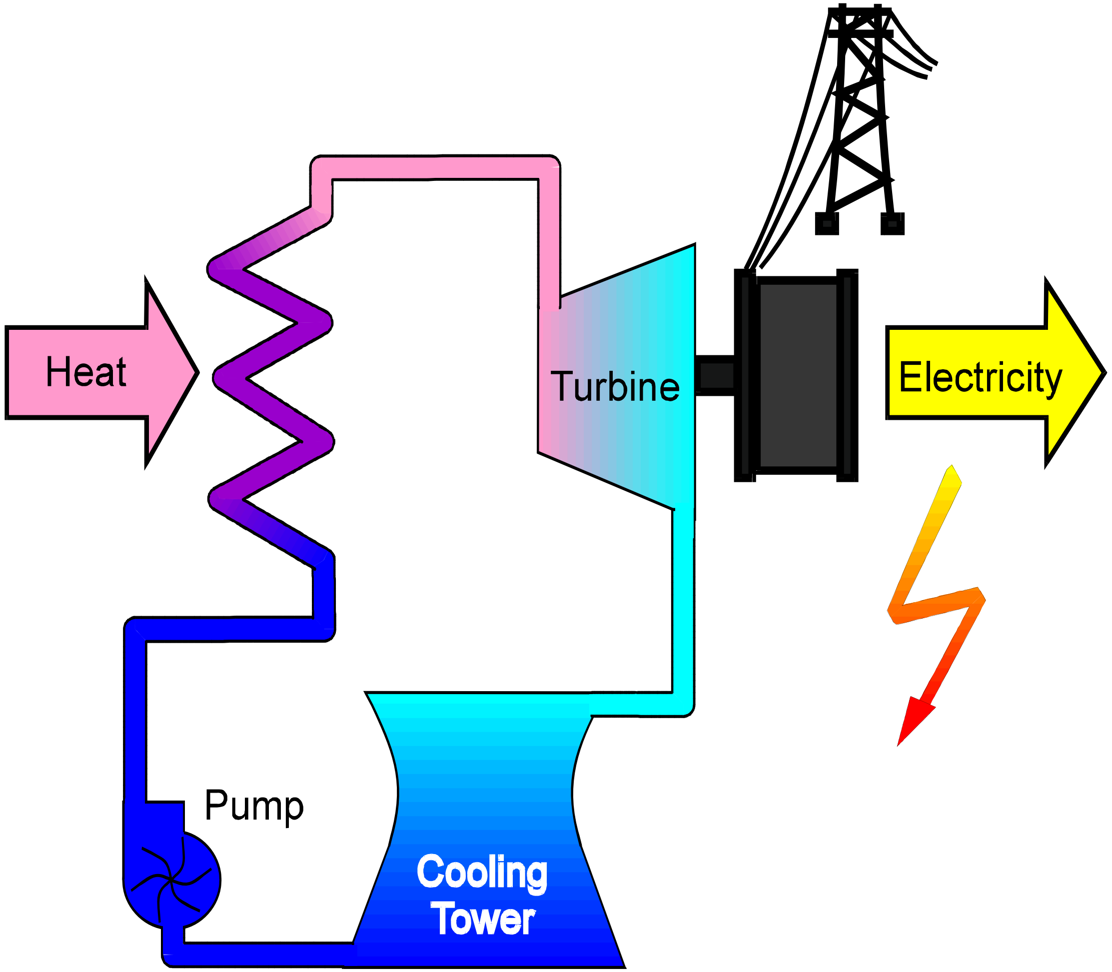
Outline:

- Solar Energy Storage in Solar-thermal (Tower)Power Plants (STPPs)
- ThermoChemical Storage (TCS) principles
- Demonstration: the Restructure Storage
- Some new ideas on redox-oxide-based porous ceramics for TCS and sulfur based TCS in STPPs
- Conclusions, current and future work

DLR's Solar Tower, Jülich, Germany

What is CSP ?

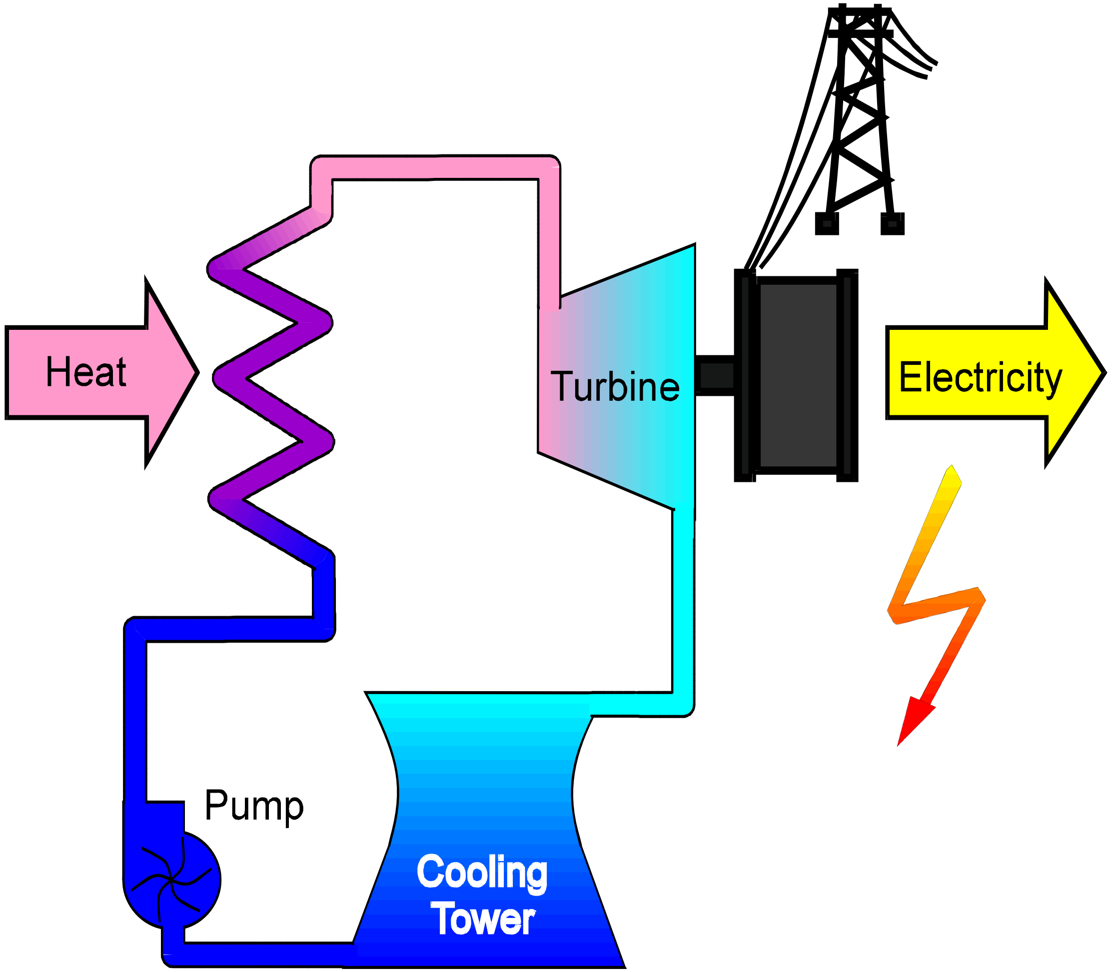




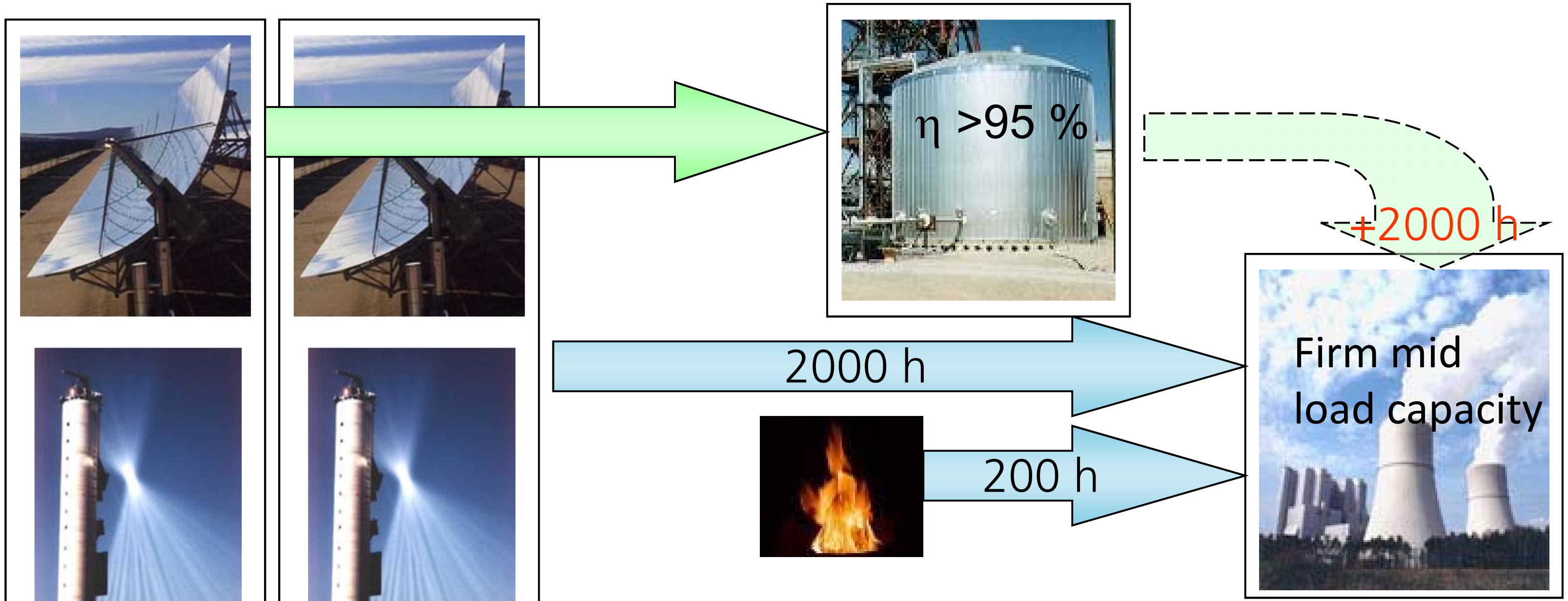
Conventional power plants

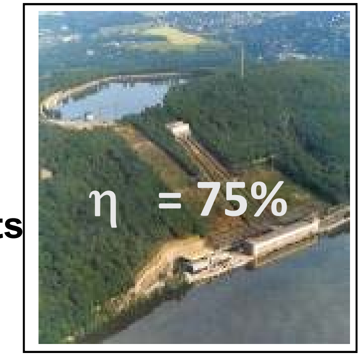
What is CSP ?

Solar thermal power plants



Thermal Storage vs. Electric Storage





CSP with storage and fossil hybridisation can provide all 3 components
Thermal storage economically favorable

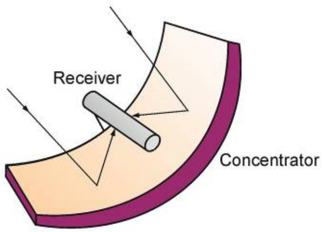
Thermochemical heat storage can provide very high energy storage densities

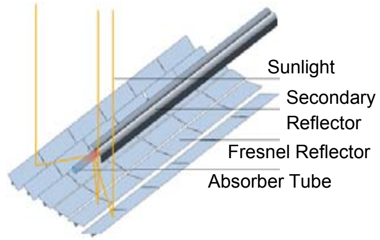
Technology	Energy Density (kJ/kg)
Gasoline	45000
Sulfur	12500
Cobalt Oxide	850
Molten Salt (Phase Change)	230
Molten Salt (Sensible)	155
Lithium Ion Battery	580
Elevated water Dam (100m)	1

- **High energy densities with low storage cost**
- **Ambient and long term storage**
- **Transportability**

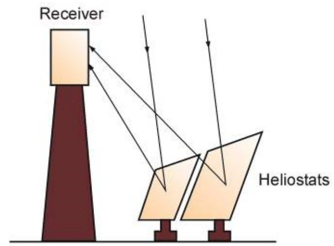
Concentrator Options for CSP Technology

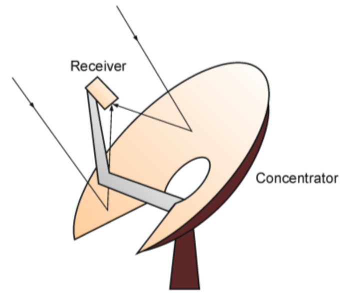
line concentrators





point concentrators





Technology	Peak solar to electricity conversion efficiency	Annual solar-to-electricity efficiency	Water consumption, for wet/dry cooling (m^3/MWh)	Land use (m^2/MWh/a)
Parabolic troughs	23-27%	15-16%	3-4 / 0.2	6-8
Linear Fresnel systems	18-22%	8-10%	3-4 / 0.2	4-6
Towers (central receiver systems)	20-27%	15-22%	3-4 / 0.2	8-12

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Solar Towers

On the Web:

http://www.ivanpahsolar.com/
http://www.psa.es/webeng/index.php
http://www.torresolenergy.com/TORRESOL/home/en
http://www.solarreserve.com/en/global-projects/csp/crescent-dunes
http://www.abengoasolar.com/web/en/plantas_solares/plantas_para_terceros/espana/

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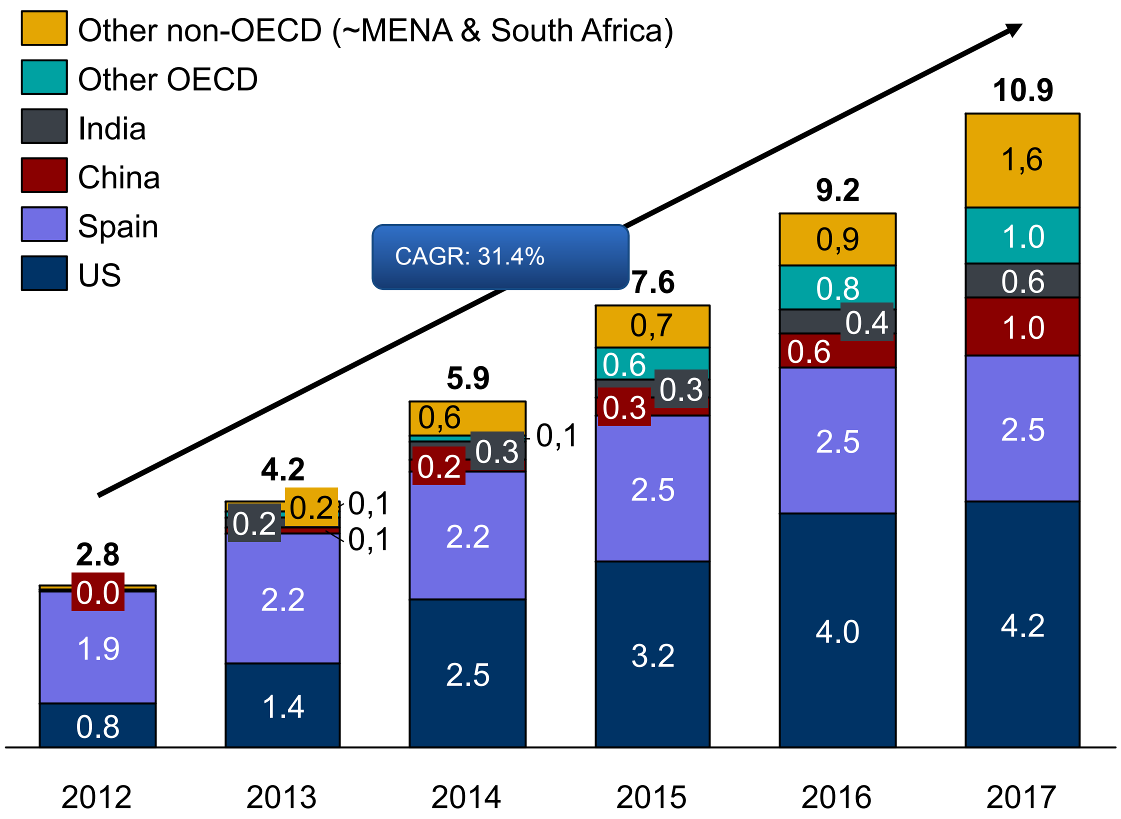
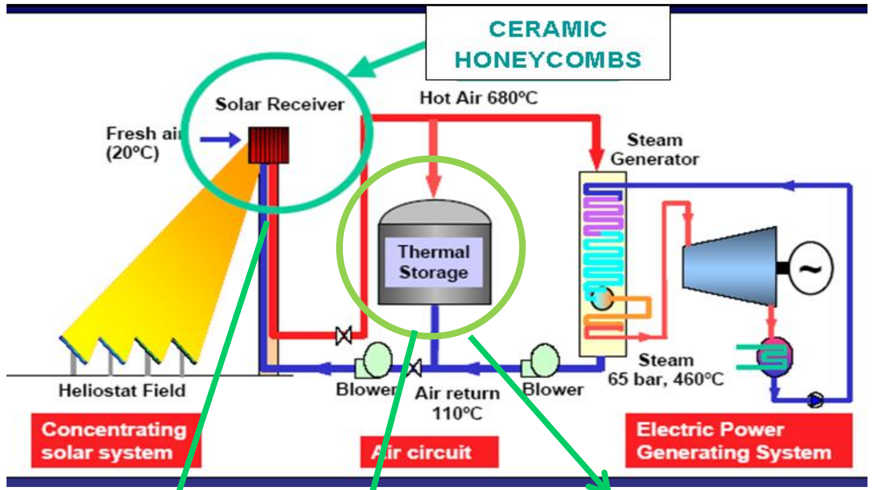
CSP Market Development according to IEA



Air-operated CSP Plants (Solar Tower Jülich/STJ)

- HTF: Air at atmospheric pressure, heated up to about 700ºC and then powering a steam generator.

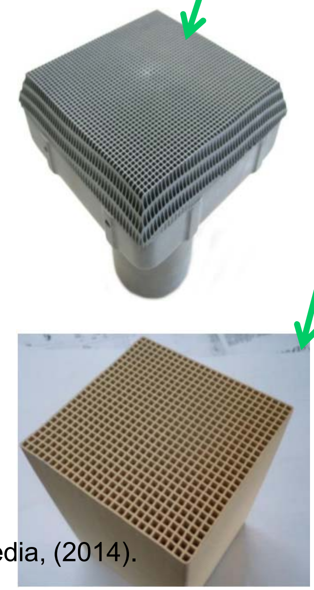
  - Sensible heat storage : TES by temperature increase (cp ΔT)

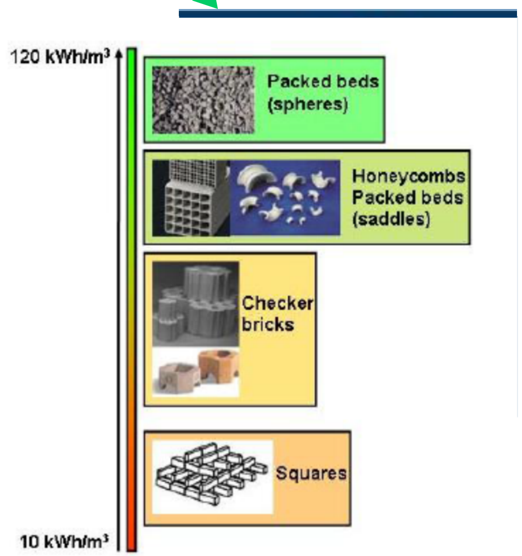


Storage design specifications	
Inlet Temperature (Charge/ Discharge)	680 °C / 120 °C
Outlet temperature (Charge/Discharge)	680-640 °C 120-150 °C
Charge mass flow	9.4 kg/s
Discharge heat rate	5.7 MWth
Full load discharge period	1.5 h
Pressure loss	< 1500 Pa

Table 2 Inventory

Honeycombs	60 x 60 cells
Brick dimensions	150 x 150 x 150 (mm)
Material	Alumina porcelain (C130)
Bulk density	2700 kg/m^3
Specific heat capacity	0.88 kJ/(kg K)
Thermal conductivity	2.1 W/(m K)
Heating surface	1180 m^2/m^3
Free cross section	69%





S. Zunft, et al.:SolarPACES, (2009); (2010); JSEE (2011); Energy Procedia, (2014).

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ThermoChemical Storage (TCS)

Reaction	No	ΔH (kJ/mol_{react})	T (°C)
$NH_3 + \Delta H \leftrightarrow \frac{1}{2} N_2 + 3/2\ H_2$	(1)	49	593
$Ca(OH)_2 + \Delta H \leftrightarrow CaO + H_2O$	(2)	100	521
$CaCO_3 + \Delta H \leftrightarrow CaO + CO_2$	(3)	167	896
$2\ Co_3O_4 + \Delta H \rightarrow 6\ CoO + O_2$	**(4)**	**202**	**890**

- **HSM: NH_3, Solids: $Ca(OH)_2$, $CaCO_3$, Co_3O_4 respectively.** **HTF: ?**
- Among the gas-solid reactions, mentioned above "… Oxide based systems have an advantage because air is used as both the heat transfer fluid and the reactant which eliminates the requirements to either store CO_2 or to evaporate water in the other TCS alternatives…".

From TES with sensible heat to TCS with redox oxides

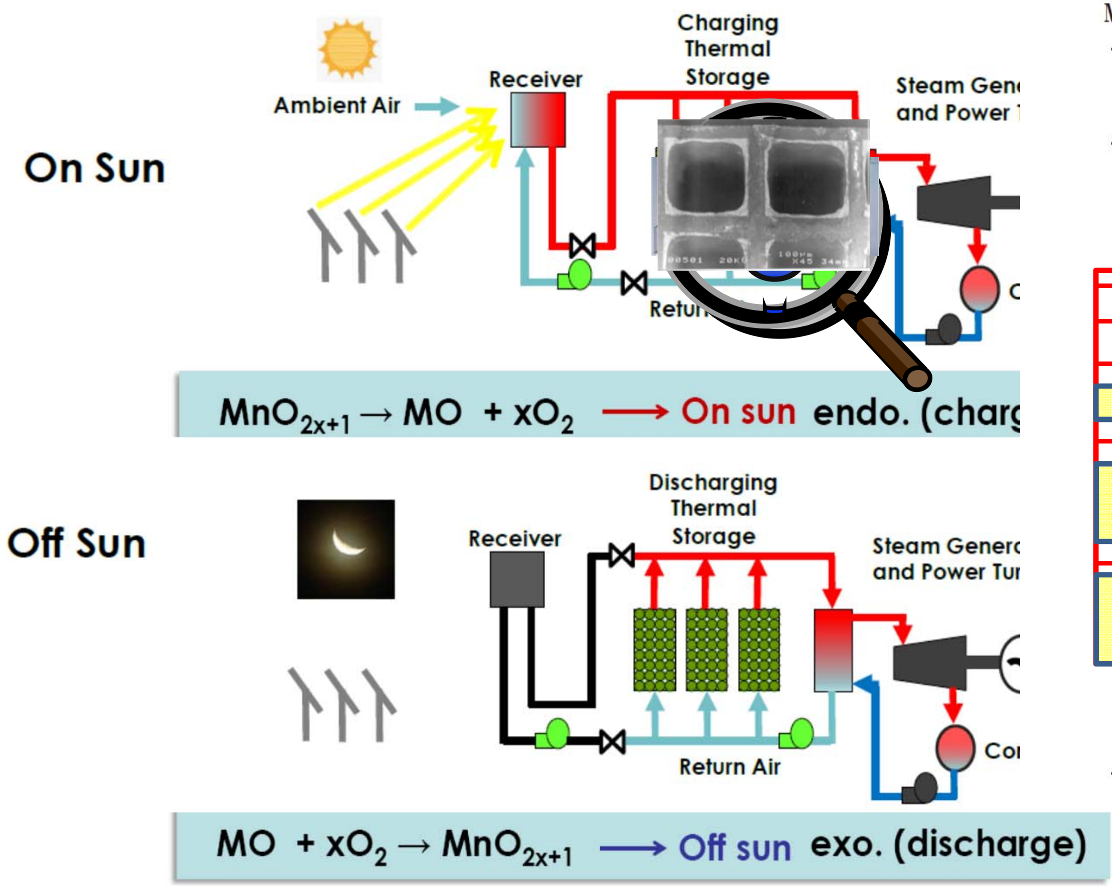


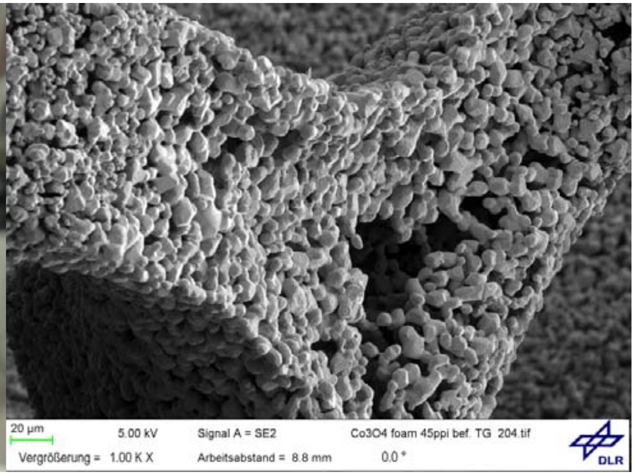
Table 2.1
Metal Oxide Systems Applicable to TES Based on Thermodynamics Considerations

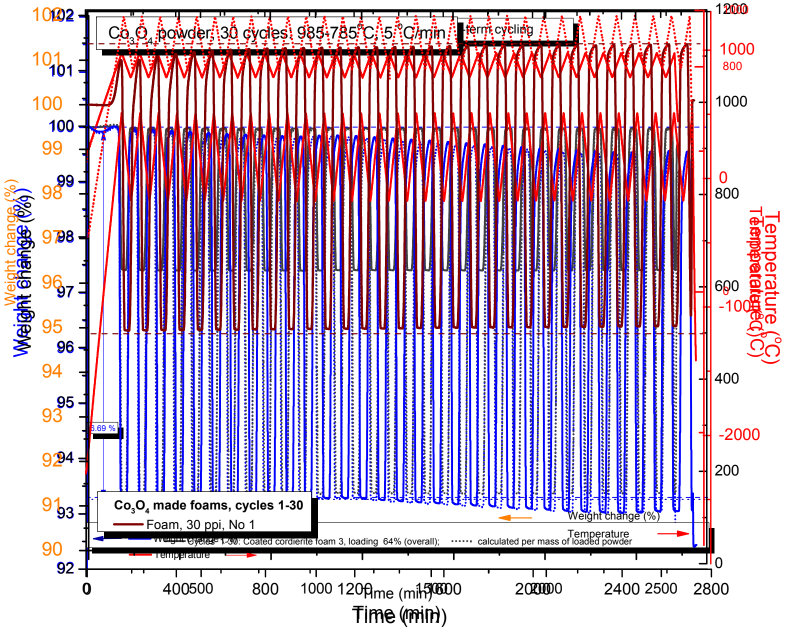
Reaction				Temperature (°C)	ΔH (kJ/mole oxide)	Storage Density (kJ/kg)
Cr_5O_{12}	→	$2.5Cr_2O_3$	$+ 2.25O_2$	110	126.0	279
$2Li_2O_2$	→	$2Li_2O$	$+ O_2$	150	68.2	1483
$2Mg_2O$	→	$2MgO$	$+ O_2$	205	21.8	505
$2PbO_2$	→	$2PbO$	$+ O_2$	405	62.8	262
$2PtO_2$	→	$2PtO$	$+ O_2$	420	62.8	277
$2Sb_2O_3$	→	$2Sb_2O_4$	$+ O_2$	515	92.5	286
$4MnO_2$	→	$2Mn_2O_3$	$+ O_2$	530	41.8	481
$6UO_3$	→	$6U_3O_8$	$+ O_2$	670	35.2	123
$2BaO_2$	→	$2BaO$	$+ O_2$	885	72.5	474
$2Co_3O_4$	→	$6CoO$	$+ O_2$	890	202.5	844
Rh_2O_3	→	Rh_2O	$+ O_2$	970	249.2	981
$6Mn_2O_3$	→	$4Mn_3O_4$	$+ O_2$	1000	31.9	202
$4CuO$	→	$2Cu_2O$	$+ O_2$	1120	64.5	811
$6Fe_2O_3$	→	$4Fe_3O_4$	$+ O_2$	1400	79.2	496
$2V_2O_5$	→	$2V_2O_4$	$+ O_2$	1560	180.7	993
$2Mn_3O_4$	→	$6MnO$	$+ O_2$	1700	194.6	850

General Atomics: GA–C27137: THERMOCHEMICAL HEAT STORAGE FOR CONCENTRATED SOLAR POWER THERMOCHEMICAL SYSTEM REACTOR DESIGN FOR THERMAL ENERGY STORAGE ; Phase II Final Report, 2011

Co_3O_4 /CoO: TGA

- Co_3O_4 can operate in a quantitative, cyclic and fully reversible reduction/ oxidation mode within 800-1000°C (950°C).
- As powder, coated on honeycombs/ foams or shaped in foams.

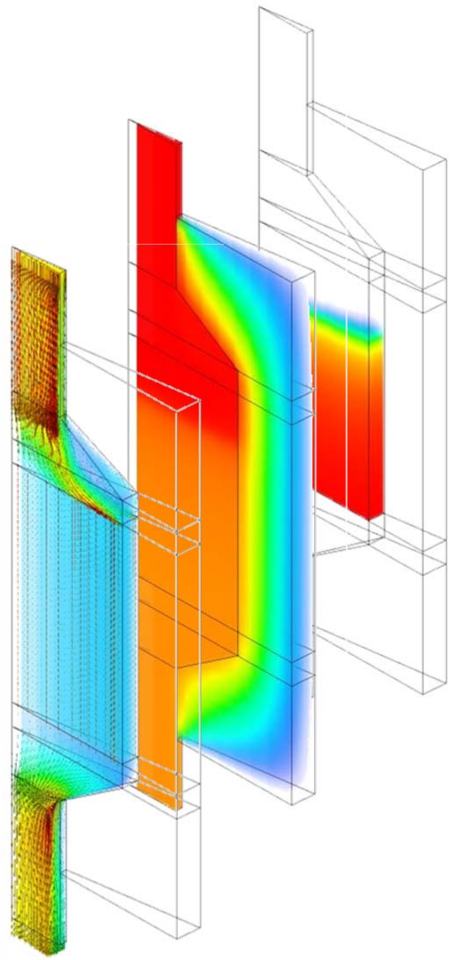


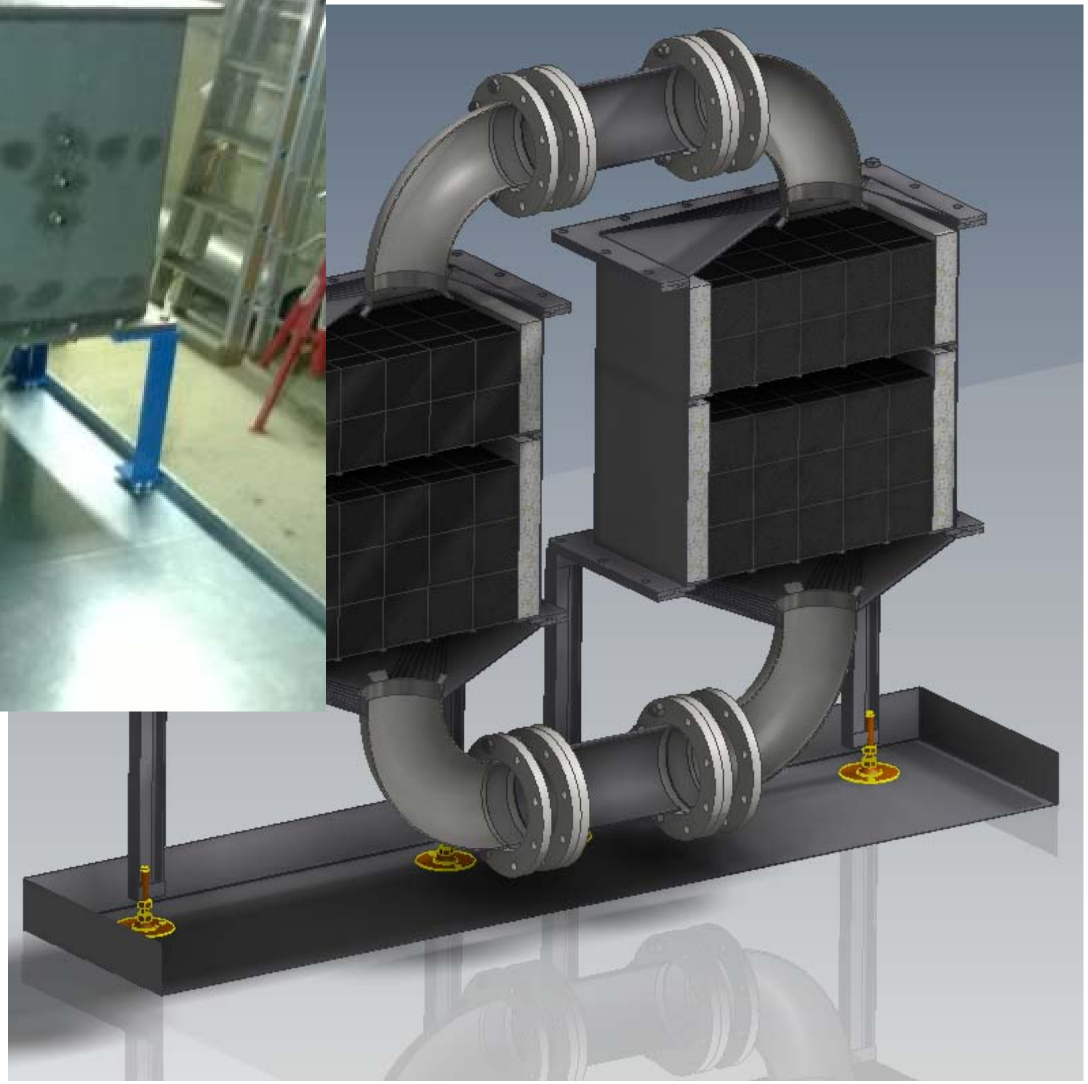


Agrafiotis, Roeb, Schmücker, Sattler, Solar Energy, (2014), (2015).

Numerical modelling of the reactor

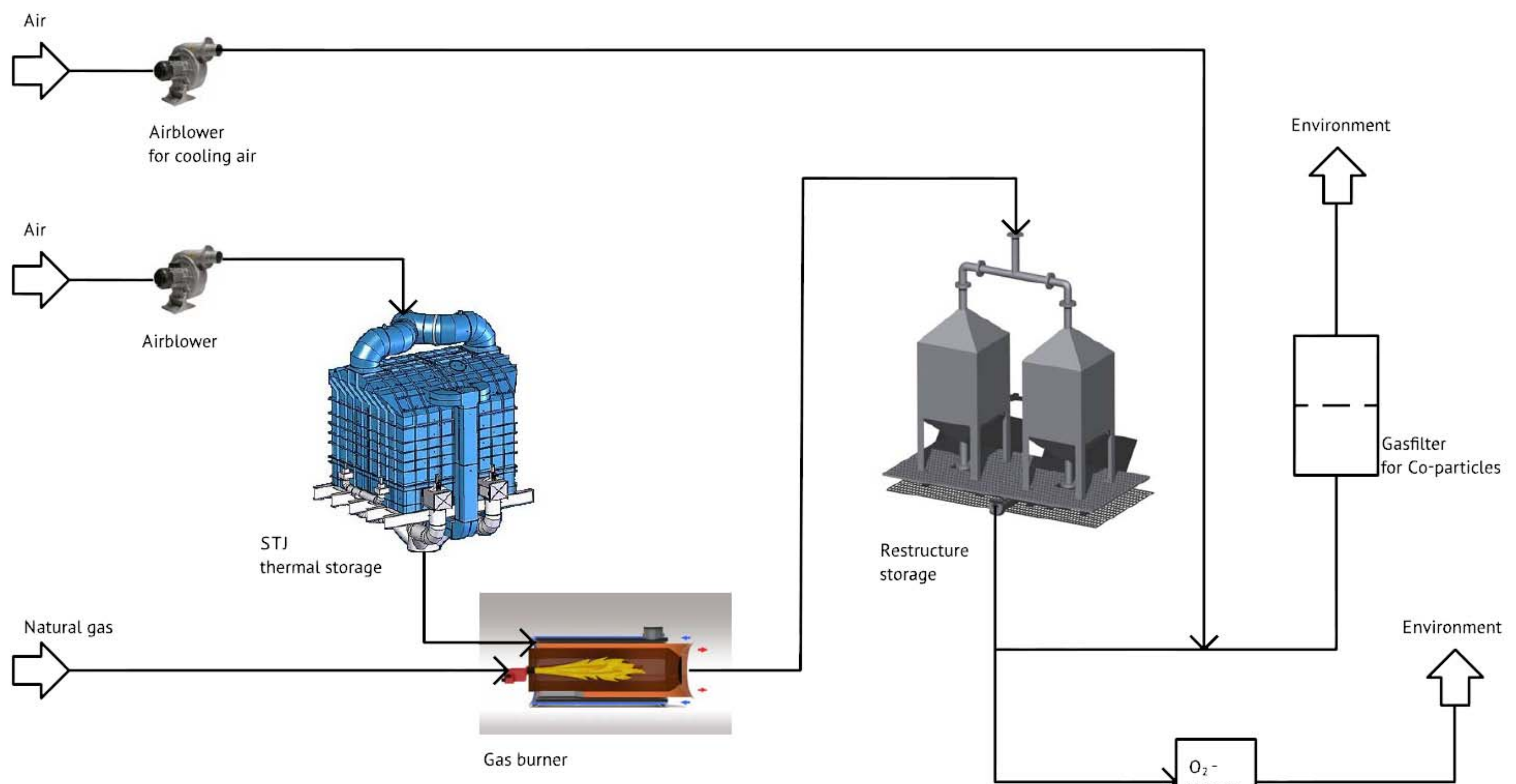
- gas flow – heat transfer – chemical reaction were modeled
- kinetics model from experimental data was implemented
- predict a cycle
- define the optimal reactor geometry

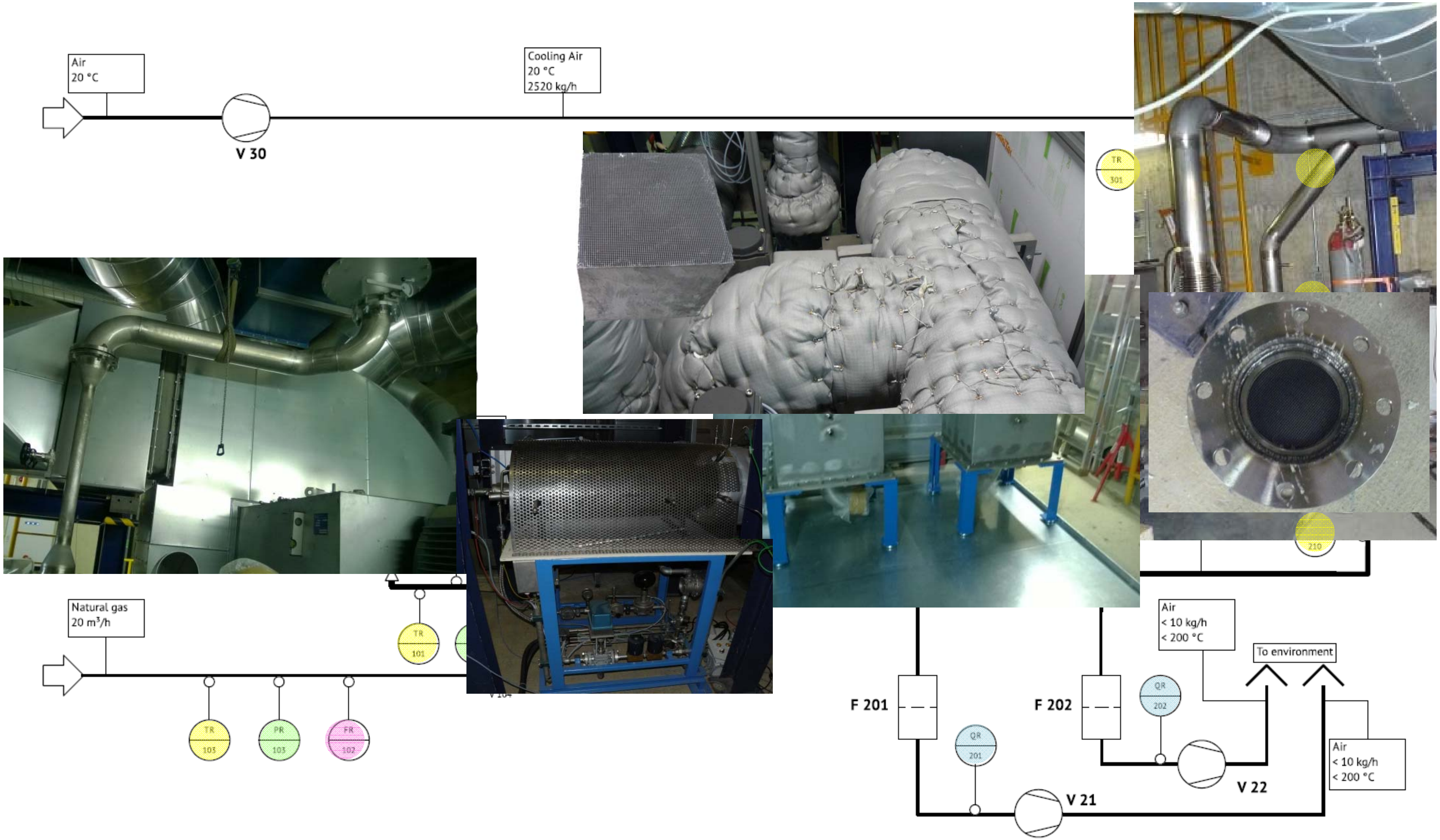




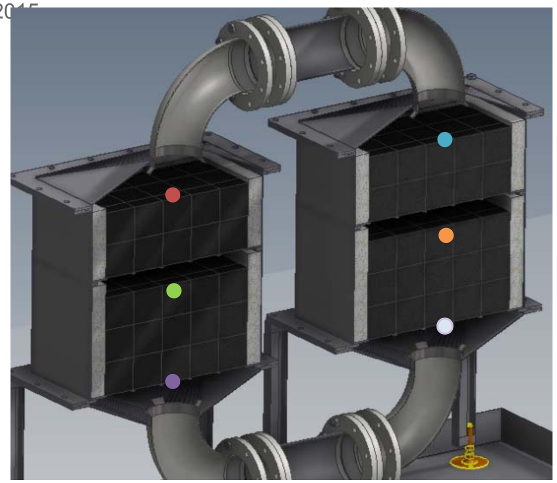
existing solar facility

Implementation in an existing solar facility



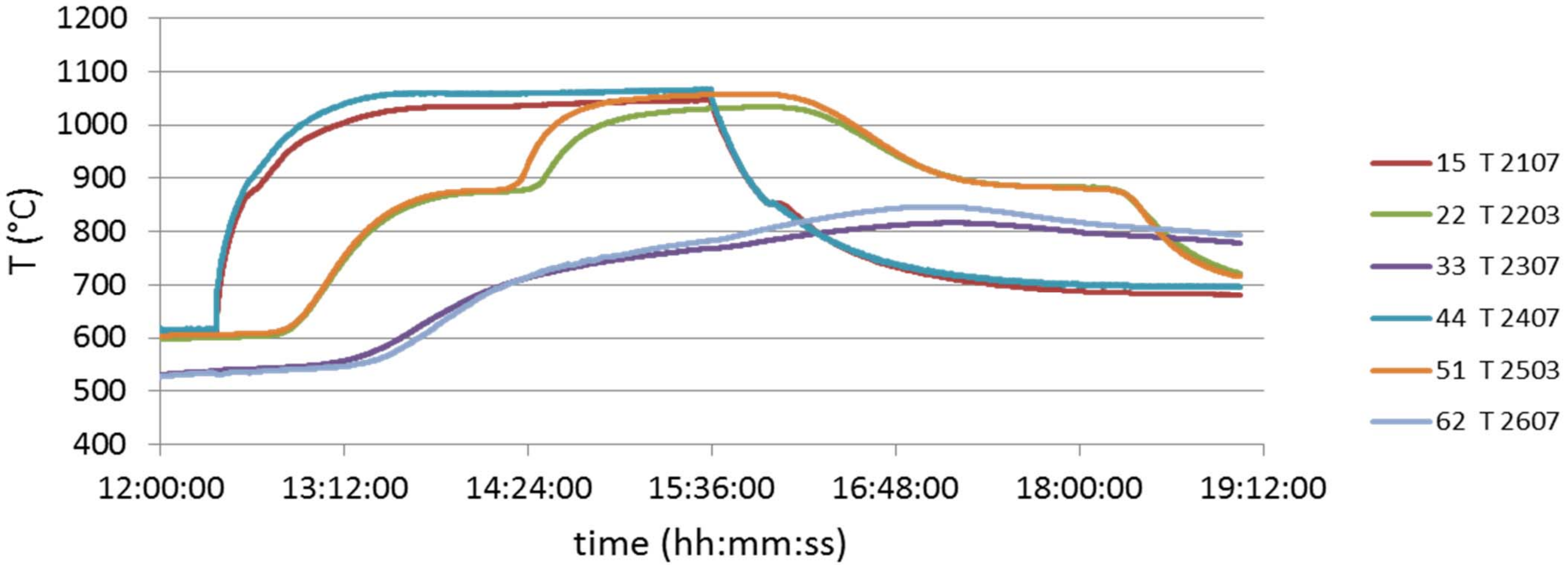

Air
20 °C
V 30
Cooling Air
20 °C
2520 kg/h
TR
301
210
Natural gas
20 m³/h
TR
101
TR
103
PR
103
FR
102
Air
< 10 kg/h
< 200 °C
To environment
F 201
F 202
QR
202
QR
201
V 22
V 21
Air
< 10 kg/h
< 200 °C

Chemical Tests



evidence of a plateau due to chemical reaction

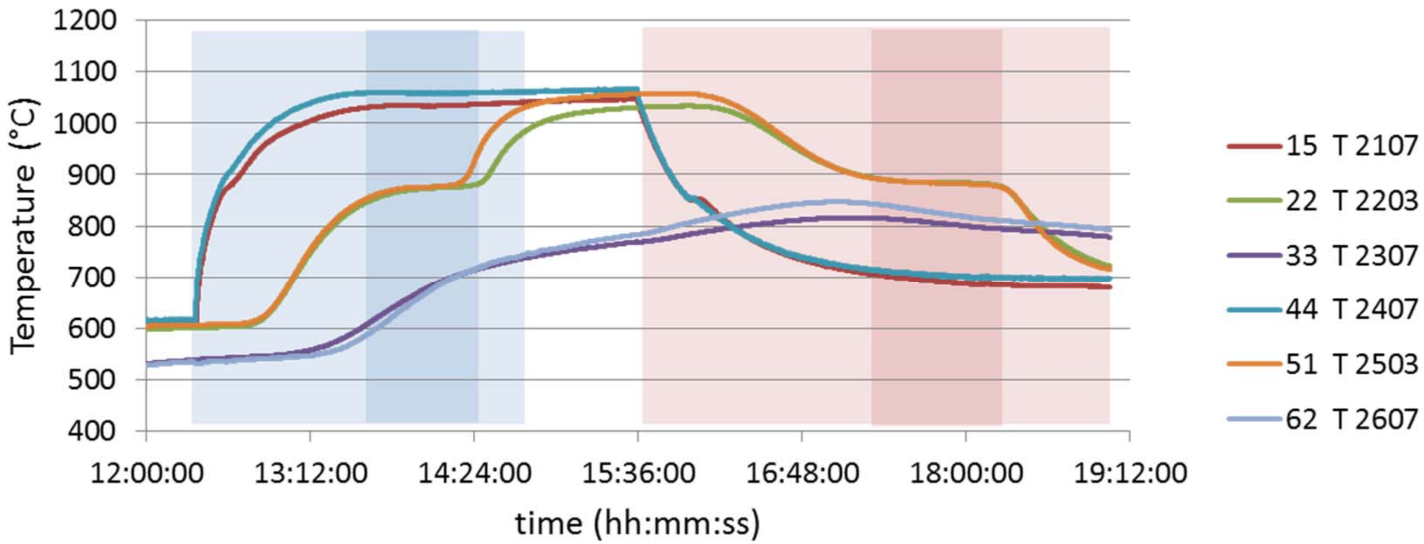
similar behavior of 2 chambers



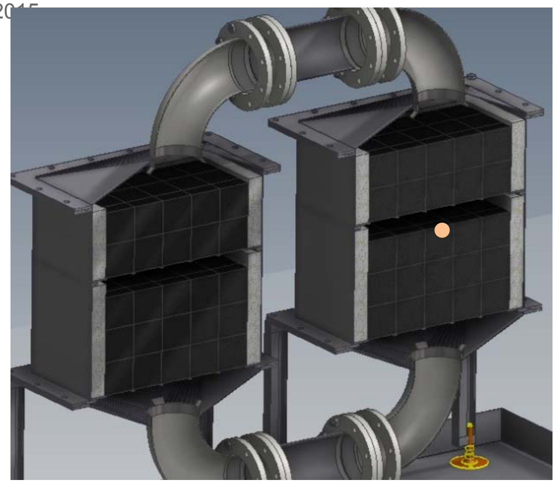
Chemical Tests

considering half of one chamber (≈25kg cobalt)

	Energy stored (kWh)	Average Power (kW)	time	at constant temperature
Charge	38	11.2	3.5 h	1 h
Discharge	32	9.6	3.25 h	1 h

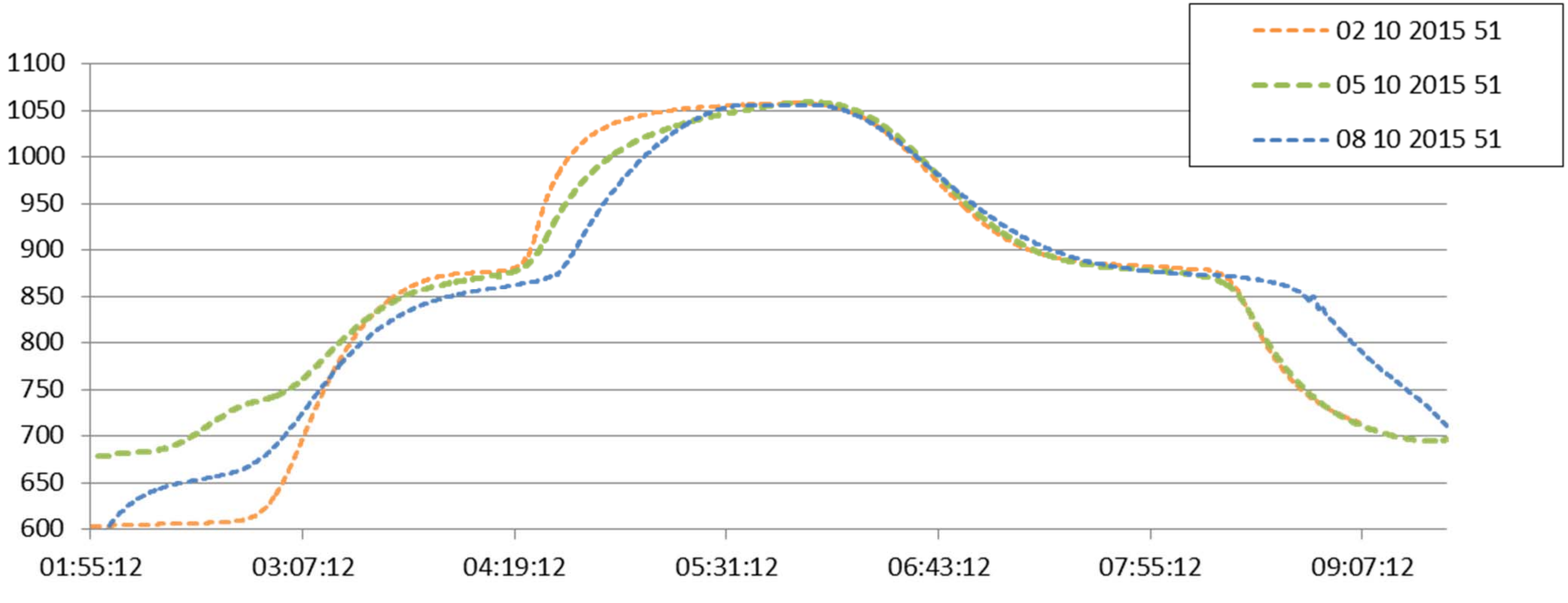


Chemical Tests



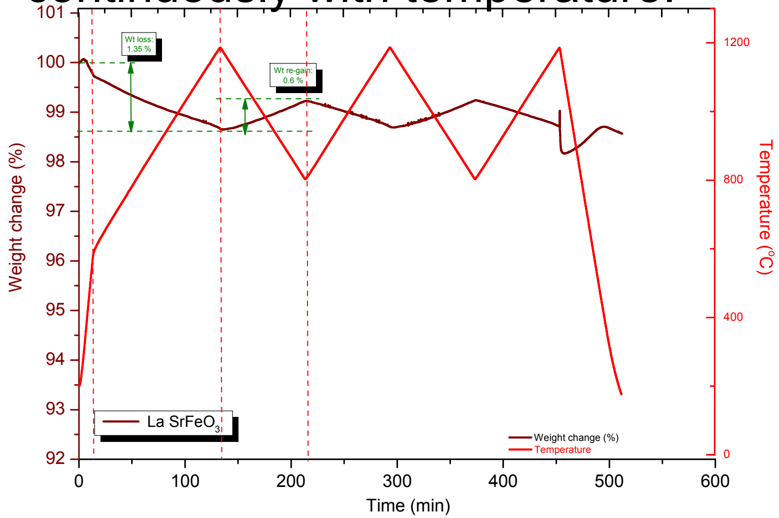
3 complete cycles:

- reproducible results
- material doesn't loose storing capacities in 3 cycles

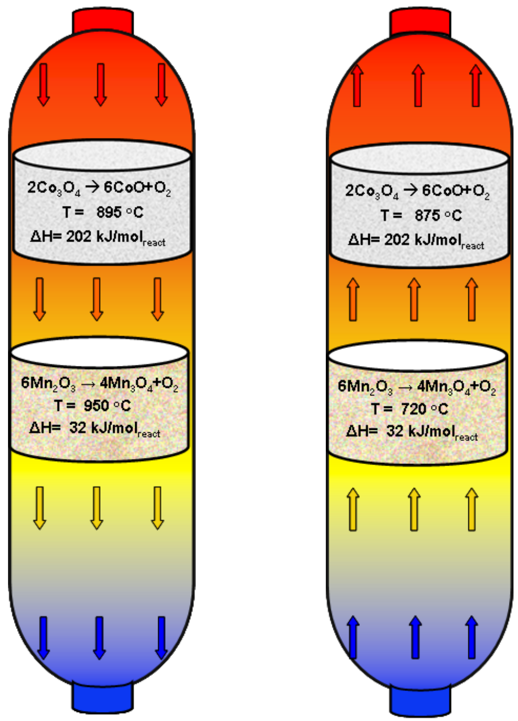


Cascaded ThermoChemical Storage (CTCS)

- CuO/Cu_2O: reduction temperature very close to m.p. of Cu_2O (shrinkage and sintering).
- BaO_2/BaO: BaO reacts with CO_2 present in air to $BaCO_3$
- Perovskites: loose/gain (little) weight continuously with temperature:



Reaction	ΔH (kJ/mol)	T_{red} (°C)	T_{ox} (°C)
$2\ Co_3O_4 + \Delta H \rightarrow 6\ CoO + O_2$	202.5	895	875
$6\ Mn_2O_3 + \Delta H \rightarrow 4\ Mn_3O_4 + O_2$	31.9	950	720

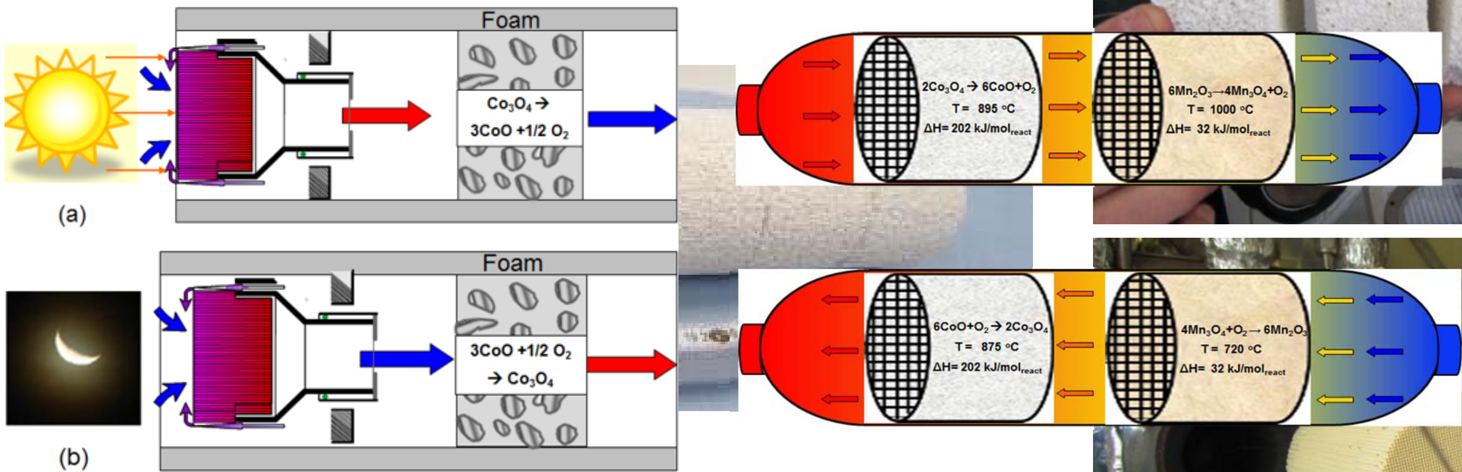


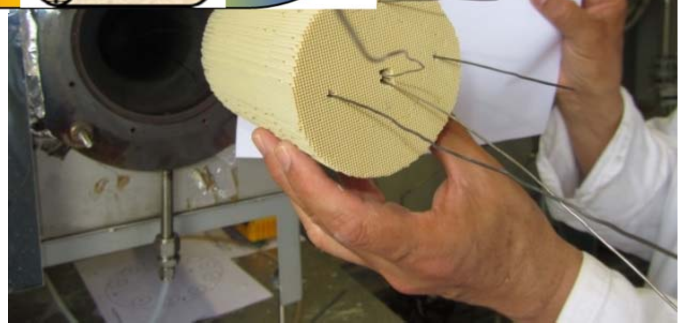
Solar campaigns: comparative testing of two storage module types

- **3 Cordierite foams**

30 ppi; BYLIM

Length = 12 cm





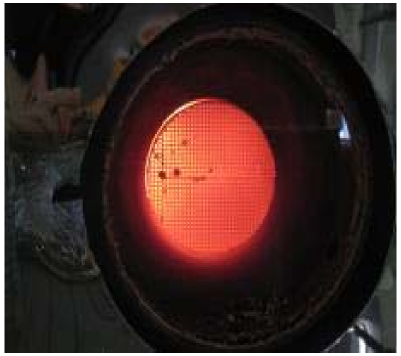
- **1 Cordierite honeycomb**

400 cpsi; NGK

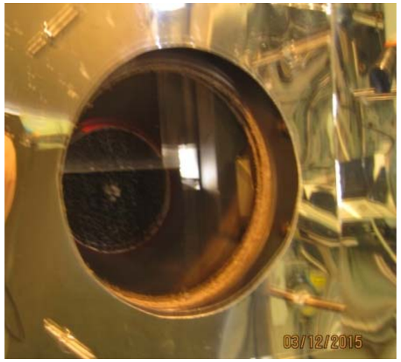
Length = 12 cm

Comparative testing of three SiC receivers (190 slm)

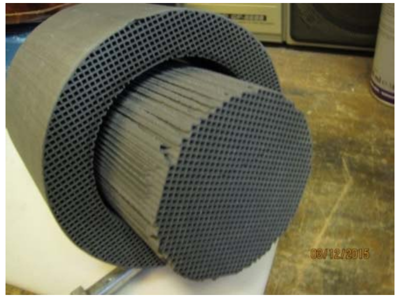
SiSiC honeycomb
90 cpsi; Schunk
Weight ≈1404 g
Length = 15 cm



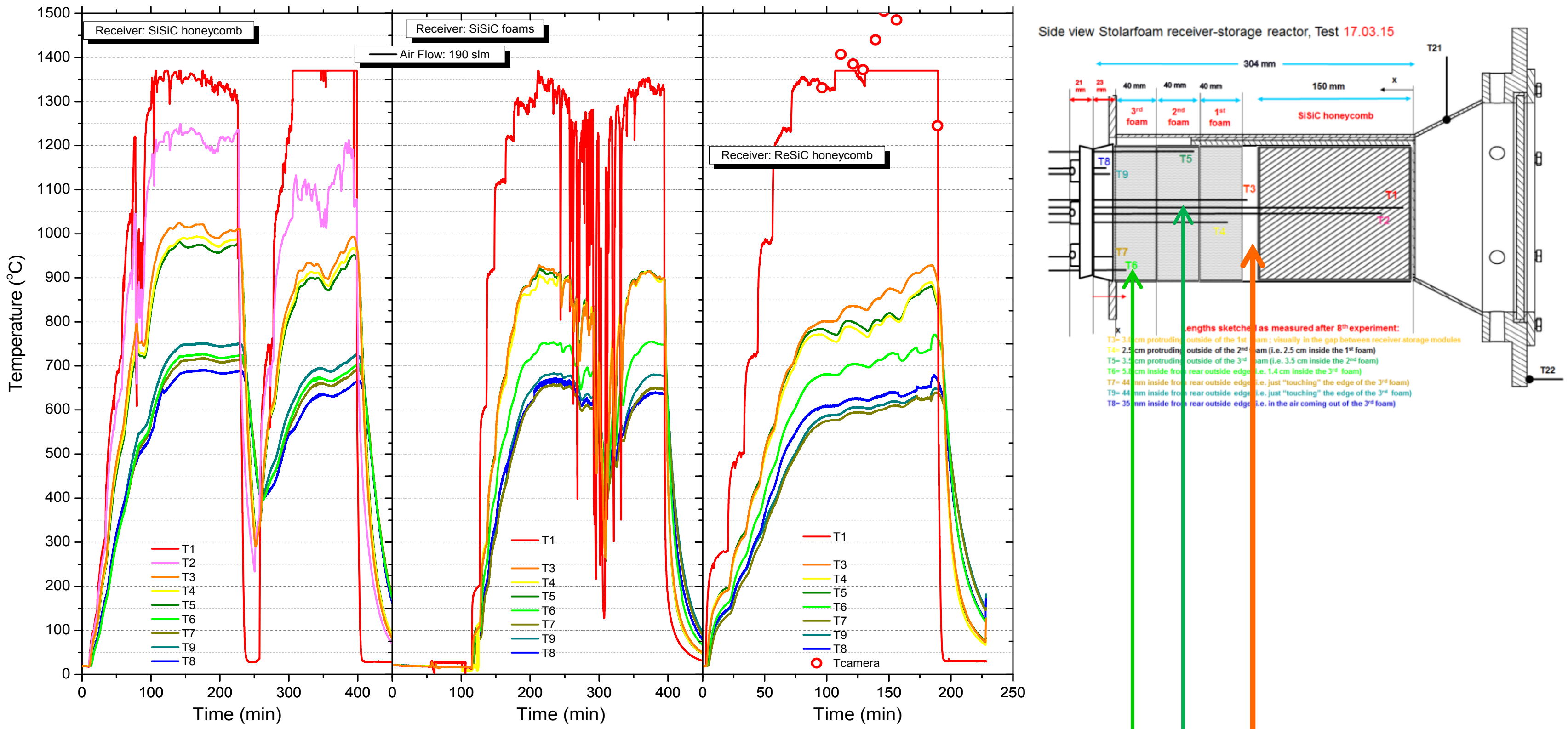
3 SiSiC foams
10 ppi; ERBICOL
Weight ≈ 246 g
Length = 12 cm



ReSiC honeycomb
90 cpsi; Stobbe TC
Weight ≈ 584 g
Length = 10 cm

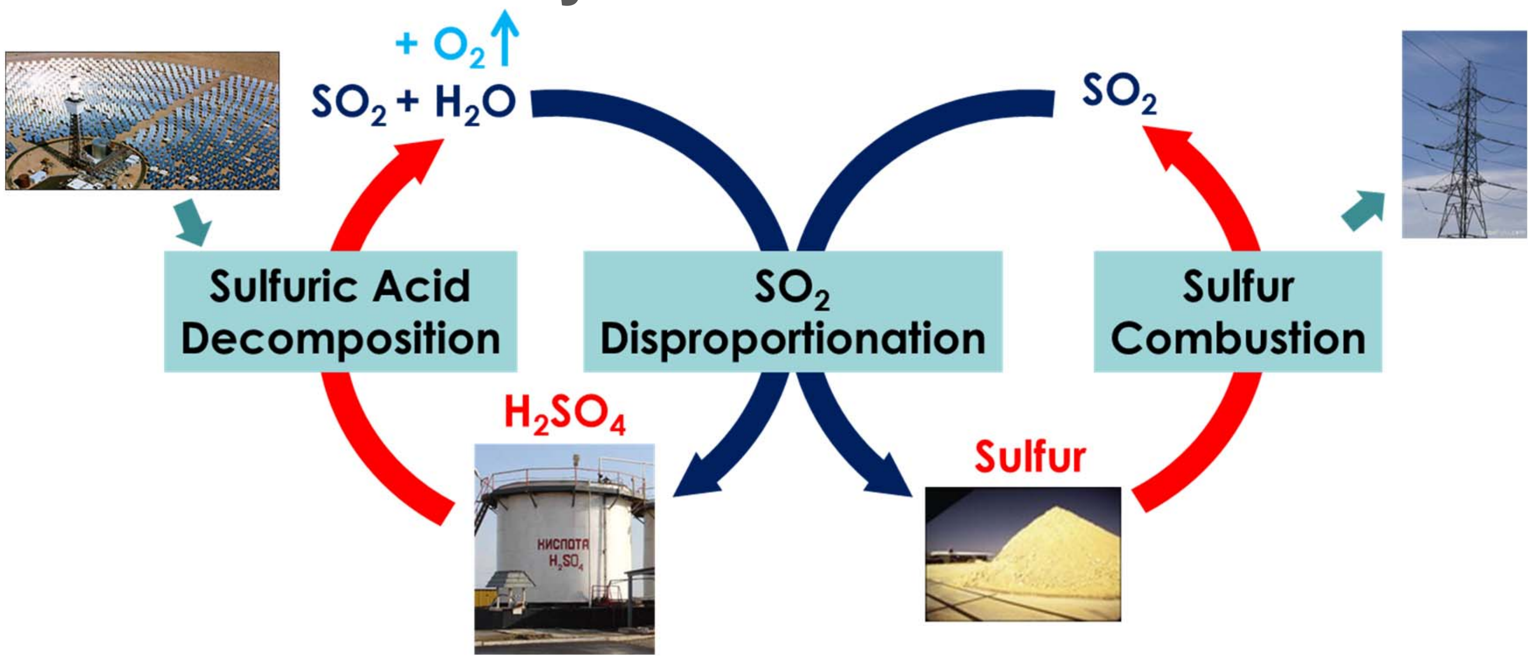


Comparative performance of SiC receivers tested



T3≈1030°C	T3≈930°C	T3≈930°C
T5≈ 975°C	T5≈915°C	T5≈875°C
T6≈ 725°C	T6≈755°C	T6≈775°C

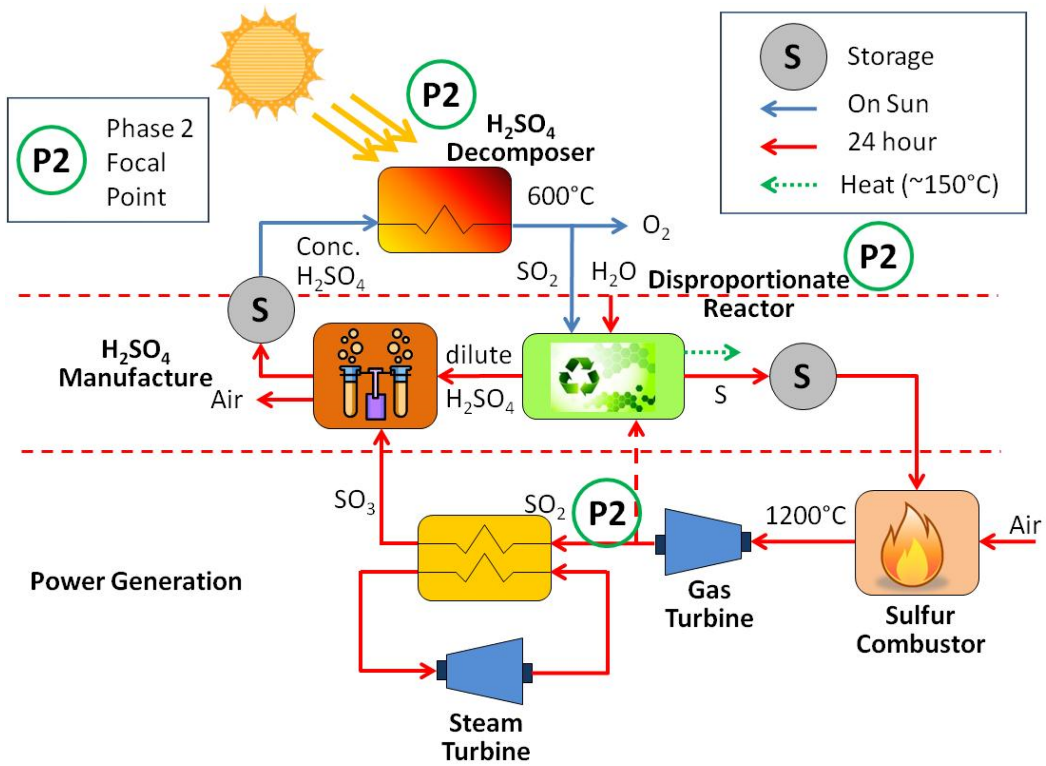
Solar energy can be stored in elemental sulfur via a three step thermochemical cycle



	Reaction	Temp (°C)
H_2SO_4 Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + O_2(g) + 2SO_2(g)$	800
SO_2 Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(l)$	150
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	1200

An improved flowsheet was established based on modeling and experimental data from Phase I

- **Plant design incorporated established processes from sulfuric acid manufacturing plant**



DOE Metric	LCOE (¢/kWh_e)
DOE Target	6.5
CSP w/Sulfur Storage	8.1*

***SAM (NREL) using 2012 costs**

- **Storage cost is < $2/kWh**
- **LCOE is ~6¢/kWh_e based on proposed Sunshot targets**

Achievements

- Thermochemical storage is an efficient way for the operation of high temperature solar-thermal power plants
- A demonstrator with two times 50 kg CoO is presently tested successfully at the solar tower of DLR in Jülich, Germany
- Cascade Thermochemical Storage will improve such systems
- Sulfur promises to be cost efficient and easy to integrate in existing processes

Outlook

- New materials are necessary as well for the sensible as for the thermochemical storage
- A further scale-up is under preparation

Acknowledgements:

- To **EU** for financing the MARIE CURIE ACTION Intra-European Fellowships (IEF) Call: FP7-PEOPLE-2011-IEF, Grant 300194: Thermochemical Storage of Solar Heat via Advanced Reactors/Heat exchangers based on Ceramic Foams (STOLARFOAM)
- To **EU** for financing the FP7-ENERGY-2011-1Grant 283015 Redox Materials-based Structured Reactors/Heat Exchangers for Thermo-Chemical Heat Storage Systems in Concentrated Solar Power Plants (RESTRUCTURE)
- To **DoE** for financing Sulfur based thermochemical heat storage for Baseload (DOE Baseload program DE-EE0003588)
- To **DLR** Programmdirektion Energie (PD-E) for funding through Project Thermochemical storage for CSP-applications based on Redox-Reactions – from materials to processes (REDOXSTORE).

SunShot U.S. Department of Energy

SEVENTH FRAMEWORK PROGRAMME

MARIE CURIE ACTIONS

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Thank you very much for your attention!

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